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The Nature of the Two-Electron Chemical Bond. III. Natural Orbitals for H_2*

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INTRODUCTION

It has previously been shown[1] that hydrogen-molecule wave functions may conveniently be represented in terms of natural orbitals.[2] In this representation, many of the approximate wave functions for H_2 in the literature were classified by the number of independent approximate natural orbitals required in the expansion and, in particular, by the occupation number of each natural orbital. It was shown that the occupation numbers were relatively invariant to a wide range of approximations to the H_2 wave function. It seemed desirable to explore the natural orbital representation in greater detail with a more accurate H_2 wave function. The results of this study are presented in this paper using the wave function for H_2 obtained by Hagstrom.[3] This function represents an expansion in terms of configurations of products over basis *orbitals.* The latter were chosen in elliptical coordinates.

Since this work was completed, Davidson and Jones[4] have made an approximate analysis of the Kolos and Roothaan[5] wave function for H_2 using an expansion of the latter function in terms of elliptical basis functions also. The results from the present expansion and that of Davidson and Jones are very similar, but since they are somewhat complementary, refer to different initial functions, and since approximations are present in each (despite the title of the Davidson–Jones paper which refers to the 'exact' wave function) it has seemed worthwhile to report on our calculations in detail.

THE WAVE FUNCTION

The Axially Symmetric Case

The basis orbitals used by Hagstrom may be defined in unnormalized form as

$$\varphi = \xi^n \eta^j e^{-\zeta\xi} e^{-\tau\eta} [(\xi^2 - 1)(1 - \eta^2)]^{|m|/2} e^{im\varphi} . \quad (1)$$

Of course (see Hagstrom[3]), when $\tau \neq 0$, these orbitals are not symmetry adapted, and one should use either sinh $\tau\eta$ or cosh $\tau\eta$ for the exponential dependence on η. This was done in Hagstrom's paper, and the results given here refer specifically to this modification for the $\tau \neq 0$ case.

For $m = 0$, the axially symmetric case, the individual configurations fall into types:

$$(\sigma_g,\sigma_g) = \sigma_g(1)\sigma_g(2) \quad (2)$$

$$(\sigma_g,\sigma_g') = \sigma_g(1)\sigma_g'(2) + \sigma_g'(1)\sigma_g(2) \quad (3)$$

$$(\sigma_u,\sigma_u) = \sigma_u(1)\sigma_u(2) \quad (4)$$

$$(\sigma_u,\sigma_u') = \sigma_u(1)\sigma_u'(2) + \sigma_u'(1)\sigma_u(2) . \quad (5)$$

No cross terms of the type (σ_g,σ_u) occur because these are not of the correct symmetry for the ground state of H_2, ${}^1\Sigma_g^+$.

In Table I are listed the expansion coefficients over symmetrized orbital products of the types mentioned above. Two functions are listed, one utilizing basis orbitals with $\tau = 0$, the other with basis orbitals having $\tau = 0.7$. Each function (hereafter labeled I and II, respectively) has 21 configurations identified by the values taken by n, j, n', j' in each.

The two functions, when judged by the coefficients of corresponding terms, seem very different. Of course, some of this difference resides in the different normalization inherent in the $\tau \neq 0$ case, but even a cursory glance shows order-of-magnitude changes in relative magnitudes of coefficients that do not arise from these factors. On the other hand, function I had an expectation value of -1.160877 H whereas function II had a corresponding value of -1.160867 H. From the similarity of the two, one suspects that the two functions are very much alike indeed.

The Axially Nonsymmetric Wave Function

If one takes the 21 terms of function I and adds 12 additional terms involving orbitals with $m \neq 0$, one obtains the wave function III of Table I. As detailed by Hagstrom,[3] each of these additional 12 terms is a

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[1] Harrison Shull, J. Chem. Phys. **30**, 1405 (1959).

[2] P.-O. Löwdin and H. Shull, Phys. Rev. **101**, 1730 (1956).

[3] Stanley Hagstrom (unpublished).

[4] E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 2966 (1962).

[5] W. Kolos and C. C. J. Roothaan, Rev. Mod. Phys. **32**, 205 (1960).

symmetry adapted function constructed from the orbital product mentioned, and contains several terms. Both π type ($m = 1$) and δ type ($m = 2$) terms were included by Hagstrom. The parameters were chosen so that $\zeta_\sigma = 1.0$, $\zeta_\pi = 1.6$, $\zeta_\delta = 2.4$, with $\tau = 0$ throughout. This function led to a total energy of -1.173128 H which compares moderately well with the Kolos and Roothaan result of -1.174448 H. The difference of 0.0013 H corresponds to only 0.9 kcal/mole or less than 1% of the *binding* energy of the H_2 molecule. Thus, one has real reason for believing that all the *major* contributing terms to the hydrogen molecule wave function have been included. Further improvements almost certainly would not introduce startling new features, but rather would make relatively imperceptible changes in those already present.

Table I. Expansion coefficients for functions I–III for H_2 ground state, $R = 1.4B$.

	I	II	III
Parameters			
ζ_σ	1.0	1.0	1.0
τ_σ	0.0	0.7	0.0
ζ_π	...	...	1.6
ζ_δ	...	...	2.4
Energy	−1.160876	−1.160868	−1.173128
Coefficients[a]			
00 00 0	−0.0037887	0.0097768	0.0198471
00 10 0	0.7831251	0.2374346	0.7391454
10 10 0	−1.2171204	−0.3529619	−1.0904790
00 20 0	−0.0661733	−0.0124179	−0.0570666
10 20 0	0.4676114	0.1293724	0.4153727
20 20 0	−0.2399662	−0.0662103	−0.2121838
00 02 0	0.1184771	0.0322608	0.1124440
10 02 0	−0.0632915	−0.0309368	−0.0500289
20 02 0	0.0326873	0.0055339	0.0288185
02 02 0	−0.0455797	−0.0188234	−0.0414525
00 12 0	−0.0293110	−0.0279961	−0.0241838
10 12 0	0.0747009	0.0350662	0.0532115
20 12 0	−0.0149941	−0.0059061	−0.0092581
02 12 0	0.0481551	0.0167674	0.0428525
12 12 0	−0.0662232	−0.0235343	−0.0577419
01 01 0	−0.1798084	−0.3740039	−0.1739298
01 11 0	0.2243633	0.4544907	0.2136638
11 11 0	−0.5387168	−1.0660162	−0.5066228
01 21 0	−0.0876663	−0.1750527	−0.0829584
11 21 0	0.2305345	0.4494511	0.2159984
21 21 0	−0.1162739	−0.2237198	−0.1079781
00 00 1			−0.1802079
00 10 1			0.2737864
10 10 1			−0.5163725
00 20 1			−0.1254296
10 20 1			0.2491153
20 20 1			−0.1488569
01 01 1			−0.0269511
01 11 1			0.0245001
11 11 1			−0.0311232
00 00 2			−0.0260503
00 10 2			0.0265872
10 10 2			−0.0336326

[a] Coefficients refer to unnormalized term groups built up from normalized basis orbitals as described in text. The five labels for each coefficient refer, respectively, to n, j, n', j', m.

It should be noted that each π, δ, etc., orbital product introduces either two or four terms in the resulting function of symmetry ${}^1\Sigma_g^+$, in contrast to the σ terms above which introduce either one or two. Thus, denoting the complex conjugate of π_u by $\bar{\pi}_u$, we would have

$$(\pi_u,\pi_u) = \pi_u(1)\bar{\pi}_u(2) + \bar{\pi}_u(1)\pi_u(2) \tag{6}$$

and

$$(\pi_u,\pi_u') = \pi_u(1)\bar{\pi}_u'(2) + \bar{\pi}_u(1)\pi_u'(2) + \pi_u'(1)\bar{\pi}_u(2) + \bar{\pi}_u'(1)\pi_u(2)\,, \tag{7}$$

in which π_u refers to a symmetry adapted orbital. The coefficients in Table I refer to *unnormalized* collections of terms, as explicitly written above, built up from *normalized* basis orbitals.

NATURAL ORBITAL ANALYSES

Natural Orbitals and Occupation Numbers

The transformation of functions I–III to natural orbital form has been sufficiently detailed elsewhere to make a summary unnecessary here.[2,6] In the natural expansion, terms of the types (3), (5), and (7), etc. are no longer present, and consequently one has a much shorter expansion in terms of the natural orbitals. For example, the 21-'term' functions I and II reduce to 8-term functions, and the 33-term function III reduces to a 15-term function. In Table II we collect the coefficients of these natural expansions (and their squares, the occupation numbers) together with the comparable results reported by Davidson and Jones as function IV.

Several comments are appropriate at this point. Since the occupation numbers and coefficients of Table II are derived from different approximate functions, there is no necessary theoretical trend to be expected except, of course, that as the wave function becomes close enough to the exact result, the occupation numbers much approach the unique exact values. Since function IV was more nearly exact to begin with, it is probable, but by no means certain, that these occupation numbers come close to the exact ones.

If one has a wave function of limited accuracy, on the other hand, one can expect that the occupation numbers of the orbital types represented are fre-

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[6] H. Shull and P.-O. Löwdin, J. Chem. Phys. 30, 617 (1959).

quently larger than the final exact values. This arises because the sum is one in either case, but in the exact function these are distributed over many more different orbitals. One can see this trend unmistakably in comparing functions I and II with either III or IV.

Table II. Coefficients and occupation numbers of the natural expansions for the ground state of H_2.

	I	II	III	IV
		Natural Orbital		
$1\sigma_g$	0.99246589	0.99248019	0.99087921	0.991058
$1\sigma_u$	−0.10632065	−0.10621056	−0.10079559	−0.099473
$1\pi_u$	...	...	−0.06589991	−0.065109[a]
$2\sigma_g$	−0.05814368	−0.05821135	−0.05506054	−0.054810
$1\pi_g$	...	...	−0.01262812	−0.011845[a]
$3\sigma_g$	−0.01172749	−0.01142289	−0.01034755	−0.009967
$2\pi_u$	...	...	−0.00950498	−0.009362[a]
$2\sigma_u$	−0.01001600	−0.00997319	−0.00943045	−0.009745
$1\delta_g$	...	...	−0.00931583	−0.009723[a]
$4\sigma_g$	−0.00847583	−0.00823981	−0.00735706	−0.006552
$2\pi_g$	...	...	−0.00330140	
$5\sigma_g$	−0.00309353	−0.00294573	−0.00287450	
$3\pi_u$	...	...	−0.00268486	
$3\sigma_u$	−0.00272593	−0.00270422	−0.00250262	
...	$2\delta_g$	...	−0.00219404	
		Occupation Numbers		
$1\sigma_g$	0.98498856	0.98501693	0.98184161	0.982195
$1\sigma_u$	0.01130406	0.01128068	0.01015975	0.009896
$1\pi_u$			0.00434280	0.004239
$2\sigma_g$	0.00338068	0.00338856	0.00303166	0.003004
$1\pi_g$			0.00015947	0.000140
$3\sigma_g$	0.00013753	0.00013048	0.00010707	0.000099
$2\pi_u$			0.00009034	0.000088
$2\sigma_u$	0.00010032	0.00009946	0.00008893	0.000095
$1\delta_g$			0.00008678	0.000095
$4\sigma_g$	0.00007184	0.00006789	0.00005413	0.000043
$2\pi_g$			0.00001090	
$5\sigma_g$	0.00000957	0.00000868	0.00000826	
$3\pi_u$			0.00000721	
$3\sigma_u$	0.00000743	0.00000731	0.00000626	
$2\delta_g$			0.00000481	
			0.99999998	0.999894

[a] These are Davidson and Jones' coefficients multiplied by $\sqrt{2}$ for direct comparison with III. J. Chem. Phys. **37**, 2966 (1962).

The latter pair differ from the former by the presence of axially nonsymmetric terms. But it is curious that the comparison between III and IV shows several anomalies in larger occupation numbers for several orbitals for IV, even though the occupation number sum is somewhat less for IV. The exceptions are $1\sigma_g$, $2\sigma_u$, and $1\delta_g$. Hagstrom[3] has already suggested that the major energetic improvement in his function will probably come through the addition of additional σ_g orbitals, and perhaps this relationship confirms his surmise.

For completeness, the natural orbitals themselves are tabulated in Table III. The forms of the individual orbitals are rather close to what one might regard as ordinary molecular orbitals for the system at hand. Of course, the first approximate natural orbital is very close indeed to the SCF orbital—the (energetically) best possible molecular orbital. But the higher natural orbitals, although bearing a resemblance in form to the excited molecular orbitals of the system, are considerably different in extent. This is fundamentally a result of the fact that they are func-

Table III. Coefficients of individual natural orbitals.[a]

Orbital	njm	I	II[b]	III
$1\sigma_g$	000	0.7751338	0.4399568	0.7634488
	100	−0.0132938	0.0042642	0.0174145
	200	0.2051068	0.1101755	0.1880335
	020	0.0840284	0.0089553	0.0871151
	120	0.0189941	−0.0054690	0.0102222
$2\sigma_g$	000	2.3481981	1.3388388	2.3935902
	100	−2.0649158	−1.1922526	−2.1663214
	200	−0.3006984	−0.1680431	−0.2408600
	020	−0.0227048	−0.1500014	−0.0116937
	120	−0.0705136	0.1033979	−0.0801900
$3\sigma_g$	000	0.2911853	−0.0851014	−0.8243185
	100	−1.5669283	0.6987698	0.4637794
	200	0.1596774	0.0079942	−0.8772411
	020	0.2424954	−0.1219611	0.4755183
	120	1.2310460	−0.7503688	0.9805583
$4\sigma_g$	000	−5.6830024	−3.0552815	−5.5930646
	100	10.532489	5.6634442	10.622112
	200	−5.6212752	−2.9915935	−5.5787836
	020	0.7602321	0.5123127	0.6339422
	120	−0.7239284	−0.5189459	−0.8823743
$5\sigma_g$	000	−1.2397225	−0.5788622	−1.3263036
	100	−0.3280373	−0.3534359	−0.1504680
	200	1.6405961	0.9870279	1.5702888
	020	3.8965410	2.2760955	3.8976451
	120	−3.7746948	−2.2025924	−3.8139986
$1\sigma_u$	010	−0.2978886	−0.4340626	−0.3238739
	110	−1.0608224	−1.4901394	−1.0297319
	210	0.3969886	0.5468881	0.3915845
$2\sigma_u$	010	3.1350537	4.5211094	3.2407999
	110	−3.6508410	−5.1262410	−3.8754268
	210	0.5372562	0.7288097	0.6665443
$3\sigma_u$	010	−5.1368978	7.4511289	5.0692557
	110	10.235268	−14.494043	−10.155563
	210	−5.9537640	8.3080743	5.9410388
$1\pi_u$	001			0.4088046
	101			0.3458974
	201			0.2752753
$2\pi_u$	001			2.3867064
	101			−1.3608281
	201			−1.0054973
$3\pi_u$	001			−8.4055843
	101			16.201853
	201			−8.5422076
$1\pi_g$	011			0.1893029
	111			0.8175903
$2\pi_g$	011			3.3775585
	111			−3.2825727
$1\delta_g$	002			−0.2658001
	102			1.2555156
$2\delta_g$	002			−4.0609476
	102			3.8711272

[a] See Table I for orbital parameters. Coefficients are those of the normalized orbitals.

[b] Coefficients of the cosh $\tau\eta$ and sinh $\tau\eta$ basis functions. See text below Eq. (1).

tionally descriptive of the *ground state* (in the present case), and, hence, have a spatial extent appropriate to the ground state of the molecule.

The comparison of the natural orbitals arising from I and III is particularly interesting. These two functions use precisely the same basis orbitals for σ functions, but the latter has, in addition, both π- and δ-basis orbitals. The σ basis in III, of course, is allowed to vary freely.

As can be seen from the table, the natural orbital coefficients for functions I and III are in remarkably close agreement with the exception of the $3\sigma_g$ orbitals. Although in this latter case $3\sigma_g$(I) and $3\sigma_g$(III) appear to be quite different, they actually have an overlap of 0.9813. The corresponding overlap between $4\sigma_g$(I) and $3\sigma_g$(III) is 0.1919, so that $3\sigma_g(\text{III}) \sim 0.98\ 3\sigma_g(\text{I}) + 0.19\ 4\sigma_g(\text{I})$.

Similarly $4\sigma_g$(I) and $4\sigma_g$(III) have an overlap of 0.9815, although in this case the coefficients are very parallel. This is an excellent example of how slight variations in basis sets make startling variations in coefficients for relatively small changes in the overall function. The relatively large change (about 2%) in natural orbitals 3 and 4 in going from calculation I to calculation III is almost certainly a result of the near degeneracy of the corresponding occupation numbers.

Energies of Truncated Functions

Löwdin and Shull showed that the ordered set of terms in the natural expansion represented term-by-term the optimum density representation of the original function. Furthermore, in the case of He at least, there seemed to exist an extraordinarily close relationship between the first such term and the ordinary Hartree–Fock solution. An analogous energetic similarity is to be expected between the truncated natural expansions of rank higher than one and the corresponding optimum energy calculations. The latter are, however, very difficult to do whereas once a complete energy calculation for the system has been done, the corresponding truncated natural orbital energies can be obtained fairly trivially.

In Table IV we have listed the energy expectation values for a number of truncated natural expansions for functions I, II, and III. A number of cases have been included in order to show the degree and rate of convergence for a rather typical wave function. Davidson and Jones (hereafter referred to as DJ) give some interesting comparative figures derived from

TABLE IV. Energies of truncated natural orbital expansions.

Calc. No.	L[a]	σ_g	σ_u	π_u	π_g	δ_g	I	II	III
1	1	1					−1.133314	−1.133350	−1.133444
2	2	2					−1.141433	−1.141472	
3	3	3					−1.142301	−1.142324	
4	4	4					−1.142631	−1.142652	
5	5	5					−1.142786	−1.142803	−1.142740
6	2	1	1				−1.151948	−1.151971	
7	3	1	2				−1.152618	−1.152633	
8	4	1	3				−1.152671	−1.152689	
9	3	2	1				−1.159405	−1.159431	
10	4	2	2				−1.159930	−1.159950	
11	5	2	3				−1.159970	−1.159994	
12	4	3	1				−1.159949	−1.159951	
13	5	3	2				−1.160462	−1.160461	
14	6	3	3				−1.160506	−1.160504	
15	5	4	1				−1.160236	−1.160234	
16	6	4	2				−1.160745	−1.160738	
17	7	4	3				−1.160787	−1.160779	
18	6	5	1				−1.160342	−1.160333	
19	7	5	2				−1.160840	−1.160828	
20	8	5	3				−1.160876[b]	−1.160868[b]	−1.160746
21	3	1	1	1					−1.162730
22	4	2	1	1					−1.169785
23	5	2	1	2					−1.170368
24	7	3	2	2					−1.171328
25	8	5	3	1					
26	11	5	3	3					−1.171742
27	12	5	3	3	1				−1.172474
28	13	5	3	3	2				−1.172593
29	14	5	3	3	2	1			−1.173058
30	15	5	3	3	2	2			−1.173128[b]

[a] L is the expansion length. For π, δ types, etc., each term in the expansion formally contributes a rank of 2 to the total rank. These terms are counted here in 'expansion length' as single terms.
[b] The energy of the complete expansion used.

Kolos and Roothaan's better wave function (at a very slightly different internuclear distance), using an expansion in terms of a finite set of basis functions larger in number than, but very similar in nature to, those used here. Since their starting function is better and the number of expansion orbitals is greater than in the present calculation, it is to be expected that their limiting values should be slightly lower than those reported here.

First, looking at the energy of the first natural orbital, we find that our calculations I–III are in excellent agreement and very close to the SCF result. Compared to -1.133444 H for III, DJ report -1.133467; both are very close to the SCF energy of -1.13356 H obtained using the same $5\sigma_g$ basis orbitals used in calculations I–III and to the value -1.133630 H obtained by Kolos and Roothaan[5] at the same internuclear distance using a slightly different basis set. The optimum SCF energy seems to be at a slightly shorter distance than the observed equilibrium distance. Kolos and Roothaan report a value of -1.133642 (interpolated) at $R = 1.375$. It is interesting to note that the first natural orbital from calculation III, including angular terms, has a lower expectation value than the first orbital from calculation I omitting the angular configurations. This phenomenon was also noticed in an earlier calculation on He.[6]

The expansion length of 2 terms is a particularly interesting case since so many of the widely known approximate functions for H_2 fall into this class. In particular, as Shull[1] has shown, the Wang function with energy -1.13910 H, the Weinbaum function (Wang + ionic terms) with energy -1.14796 H, and the Rosen function (polarized Wang function) with energy -1.1485 H, all fall in the rank 2 category with one σ_g and one σ_u natural orbital represented. This is No. 6 of Table IV where we find an energy of -1.151948 and -1.151971, respectively, for functions I and II. DJ report an energy of -1.151939, surprisingly a little above our results. This suggests that at least some of the remaining discrepancy between their function and that of Kolos and Roothaan lies in an inadequate representation of the σ_u class of orbitals. Davidson and Jones[7] in an independent calculation of correlation splitting in the hydrogen molecule obtained an energy of -1.152072 H, when they minimized the energy of the rank 2 function directly. The corresponding energy of their rank 2 function obtained by truncation of the complete variation function was -1.151943, slightly above the results reported here despite the fact that the variational energy was slightly better.

All of these functions can be expressed in "u,v" form:

$$\psi = N[u(1)v(2) + v(1)u(2)] ,$$

and, therefore, have the physical intuitional simplicity of the Heitler–London approach. At the same time, of course, they have considerably lower energy and are, hence, better representations of the bond than the cruder Wang, Weinbaum, or Rosen functions.

The only other previously reported rank 2 function with lower energy is that of Mueller and Eyring[8] using only two terms of a similar basis set in elliptical coordinates. Their reported energy of -1.154 H (computed from the published binding energy of 4.20 eV) is in error, however, as previously suggested from the occupation numbers.[1] We have recalculated the energy for this function using the published values of the parameters and have obtained instead a value of -1.14951 H. This is a negligible improvement over the result of Inui[9] (the same calculation without so-called 'ionic' terms) of -1.14930.

The limiting energies of expansions consisting of a single or a limited number of symmetry types have general interest. These form mathematically justifiable divisions of the correlation energy into types which seem to be approximately additive in many cases. Furthermore, there seems to be a relationship between those observed for H_2 and for He.[10]

The σ_g limit (calculation No. 5 of Table IV) seems to be at about -1.1428 H since our best result is very close to this. The difference between this result and the SCF result in the same calculation of -1.1334 H, may be classed as the ultimate attainable g in-out correlation energy. The total is 0.0094 H. It is interesting to compare this result with the improvements of 0.0083 (No. 6–No. 18 of Table IV), of 0.0082 (No. 7–No. 19), and of 0.0082 (No. 8–No. 20) for corresponding functions with one, two, or three σ_u terms in addition. One observes the usual diminution of improvement with an increasingly good wave function, but the value is nevertheless surprisingly constant. Probably a similar correlation energy term would result from more thorough analysis of function III, since the addition of only a single additional σ_g orbital improved this function by 0.0071 H (No. 21–No. 22). In this case, the functions contain a π_u term as well.

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[7] E. R. Davidson and L. L. Jones, J. Chem. Phys. **37**, 1918 (1962).

[8] C. Mueller and H. Eyring, J. Chem. Phys. **19**, 1495 (1951).

[9] T. Inui, Proc. Phys. Soc. Japan **20**, 770 (1938).

[10] Harrison Shull, Ann. Acad. Reg. Sci. Upsalien. **3**, 65 (1959).

In addition to this g type of in-out correlation, there is an additional in-out correlation provided by additional terms of the σ_u type after the first one. This is, however, essentially impossible to separate from left–right correlation energy since it is not clear whether the energy improvement occurs from the off-diagonal interaction with the major σ_g terms (left-right correlation) or the interaction with the major σ_u term (in-out correlation) or both. It seems most likely to be the former, however, and we lump it together with that type in the following.

The next interesting case is the limiting best function which retains only axially symmetric orbitals for basis functions. That is, the $(\sigma_g + \sigma_u)$, or Σ limit. This is the function which James and Coolidge[11] identified as the best function using only four essential coordinates [omitting r_{12} in their case, $(\varphi_2 - \varphi_1)$ in ours]. Whereas James and Coolidge reported -1.1577 H for this limit, we find -1.160876 H for our best function of this type (No. 20). The total Σ correlation energy in III is, therefore, 0.0276 H, somewhat higher than but still close to the figure of 0.0239 H predicted from a symmetrical division of correlation energy of the He atom.[10] Actually, the total Σ correlation energy is probably somewhat greater than this ($\sim$0.0286 H) since it seems clear that the chief deficiency of function III is in the $\sigma\sigma$ terms. DJ[7] report a Σ-type function with energy -1.161695 H.

Comparing calculations No. 20 and No. 26, we find an improvement in adding π_u terms of 0.0110 H. An additional contribution of 0.00085 H results from adding π_g terms (No. 26–No. 28), for a total π correlation energy contribution of about 0.012 compared to 0.015 suggested from He.[10] Clearly left-right correlation in H_2 is more important than is computed from the united atom description of the molecule, and correspondingly up-down or axial correlation is less important. This is a not unreasonable result considering the increasing importance that left-right correlation has with increasing internuclear distance and the decreasing importance of angular correlation for large distances.

Finally, we should mention the Δ term (28–30) of 0.000535 H. DJ obtained an improvement of 0.000477 H upon adding their first δ_g term. In He, terms of this type contribute 0.00116 to the correlation energy, so once again we see the decreased importance of axial correlation in H_2 as compared to the same type of correlation in He. It should be noted, however, that the total correlation energy is very nearly the same in the two cases, and He may still be retained as a very good model for H_2.[12]

As Davidson and Jones point out, there is a noticeable break in the energy contribution produced by additional natural orbitals after the fourth term has been added. This four term function (No. 22) in our case had an energy of -1.169785 H. DJ report a slightly better limiting energy of -1.169969, which is a remarkably good result for such a simple function.

In conclusion, it can be said that the present calculations have confirmed in detail previous surmises about (a) the invariance of the natural orbital expansion, (b) its utility in wave-function comparison, (c) the similarities between He and H_2, (d) the rough additivity of correlation energies of different types. The calculations provide detailed natural orbitals which should be useful in a variety of other calculations in which one is primarily exploring the effects of a systematic rapidly convergent improvement in the nature of the wave-function expansion.

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[11] H. M. James and A. S. Coolidge, J. Chem. Phys. **1**, 825 (1933).

[12] Hagstrom (reference 3) has also considered the effect of adding φ_u basis orbitals and found that a single (φ_u, φ_u) term added to the 33-term function of Case III gave an improvement of <0.00001 H.

Discussion on Natural Expansions and Properties of the Chemical Bond

F. Harris, *Chairman*

Nesbet: What are the symmetry properties of the natural spin-orbitals?

Löwdin: A theorem was presented at the Madison Symposium in 1956 about the symmetry properties of the natural spin-orbitals stating that they are symmetry-adapted. [See P. O. Löwdin, J. Phys. Chem. **61**, 55 (1957).] The basic theorem says that, if there is a normal constant of motion Λ commuting with the total Hamiltonian $\mathcal{H}$ which is built up from one-electron operators $\Lambda(i)$ by means of the sum

$$\Lambda = \sum_i \Lambda(i)\ , \tag{1}$$

or by means of any other fundamental symmetric function of the one-electron operators, including the product $\Lambda(1)\Lambda(2)\cdots\Lambda(N)$, then the natural spin-orbitals associated with an exact or approxi-